Preparation, Characterization of Mn/Cr_2O_3 and Investigation of The Photocatalytic Degradability by UV light

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Abstract

A new photo catalyst (Mn/Cr_2O_3) was prepared by the co-precipitation method by mixing two metal nitrate include of chromium(III) nitrate [$Cr(NO_3)_3.9H_2O$] with Manganese(II) nitrate [$Mn(NO_3)_2.4H_2O$] in different values and calcinated in two temperatures (550°C & 750°C), and then determination of its effectiveness for the photocatalytic activity for the degradation of Congo red as a textile dye was done to optimize the best photocatalyst and was found that (Cat-1b-) was the best for the photodegradation of Congo red, and with removal percentage (71.93) when the concentration of Congo red was (20 ppm) with weight of catalyst (0.1 g) at room temperature. The characterization of the prepared catalysts had been carried out by the XRD & SEM and has been found that the appointed catalyst (Mn/Cr_2O_3) was successfully prepared. And then some studies had been performed to optimize the reaction effective parameters on the photocatalytic degradation of Congo red such as: catalyst weight, initial concentration of the dye solution. The best catalyst's weight was (0.1g) and the concentration of the dye was (10ppm).

Keywords: Heterogeneous photocatalytic, chromium (III) nitrate, manganese nitrate, Mn/Cr_2O_3, Congo red, XRD and SEM.

الخلاصة

تم تحضير العامل المساعد الجديد (Mn/Cr_2O_3) عن طريق استخدام طريقة الترسيب المشارك بواسطة مزج نترات لفلزين مختلفين وهما نترات الكروم الثلاثية تساعية الماء مع نترات المنغنيز الثنائي رباعية الماء وبنسب مختلفة وتم تحميصها في درجتي حرارة (550°م و 750°م), ومن ثم تم تعيين فعاليتها في التحفيز الضوئي في تكسير صبغة الكونغو الأحمر التي هي من الاصباغ النسيجية ,اذ تم تعيين العامل المساعد الافضل في التحفيز الضوئي الذي هو (Cat-1b-) حيث أعطى نسبة إزالة للصبغة (71.93%) عندما يكون الكونغو الأحمر (20ppm) ووزن العامل المساعد (0.1 غم) عند درجة حرارة الغرفة. تم تشخيص العوامل المساعدة المحضرة بواسطة جهاز حيود الاشعة السينية (XRD) و مجهر المسح الالكتروني اذ أثبت تحضير العامل المساعد بنجاح. وكتطبيق لفعالية العامل المساعد المحضر تم اجراء بعض الدراسات لتحديد العوامل المؤثرة على كفاءة التكسير الضوئي المحفز للكونغو الأحمر مثل :تـأثير وزن العامل وكذلك التركيز الابتدائي لمحلول الصبغة: اذ ان افضل وزن للعامل المساعد هو (0.1 غم) الذي أعطى أفضل نسبة تكسير لصبغة الكونغو الأحمر بتركيز (10ppm).

الكلمات المفتاحية: التحفيز الضوئي الغير متجانس، نترات الكروم الثلاثية، نترات المنغنيز، العامل المساعد(Mn/Cr_2O_3)، الكونغو الاحمر، جهاز حيود الاشعة السينية، مجهر المسح الالكتروني.

Introduction

One of the most important problems that our societies are facing in the present century is the contaminated water by the wastes of the industrial wastewater because it is highly soluble in water and need for many hours and may be many days to be degraded, so the heterogeneous photocatalytic process is one of the most important processes for the degradation of these organic or inorganic wastes [Lee (2008), Bibek (2010) and Harikumar *et al.* (2013)] , and it is considered one of the advanced oxidation processes (AOPs) Miguel (2003).

The heterogeneous photocatalytic processes had widely developed in the fields of energy liberation and environment concerns and it is defined as the addition of a catalyst to accelerate the photoreaction by generating of the hydroxyl radicals, this process nicknamed as "heterogeneous" because there are two different active phases solid and liquid. Heterogeneous photocatalytic process involves utilizing the near UV light to photo promote a semiconductor in the presence of oxygen Miguel, (2003). Under these conditions oxidizing species, either bound hydroxyl radical or free holes, are generated. So many catalysts have been used in this process, TiO_2 under solar irradiation had been used in some azo dyes (Methyl orange and Orange II) photocatalytic degradation in aqueous suspension [Vincenzo *et al.* (2002)].

So, the most important is to know how this photocatalytic process works, when the exerted light (hv) energy by a UV-lamp on a semiconductor being equal to or higher than the band gap energy of the semiconductor it will promote the electron from the valence band(VB) which is full of electrons at zero Kelvin to the conduction band (CB) which is empty at the zero Kelvin, leaving a hole in the valence band and that what is called excitons (**e^-/h^+**) then the generated electron and hole transfer to the surface of the semiconductor, where the semiconductor acts in two types of reactions, acts as a donor for electrons when the promoted electron enters in reduction reaction with the species on the surface, while it acts as an acceptor for electron when the positive hole participates in an oxidation reaction [Nicholas (2010) & Falah (2011)] Figure-1-.

Mechanisms of releasing oxidizing species:

The heterogeneous process was a very complicated process because the oxidizing pathway wasn't very clear until Jean-Marie Herrmann suggested that the heterogeneous process can be divided into five steps [Herrmann, (1999)]:

1. Transferring of reactants to the surface.
2. Adsorption of one of the reactants.
3. Reactions of the reactants in the adsorbed phase.
4. Desorption of the product(s).
5. Diffusion of the product(s) from the surface.

The hydroxyl radicals can be formed by two pathways, the hole in the valence band (h_{Vb}^+) can either react with the adsorbed water or the surface hydroxide ions (OH^-) groups on the surface of catalyst such as titanium dioxide (TiO_2) particles [Radwan A. (2005), Lomoră M. *et al.* (2011), Cheng C. *et al.* (2012)]:

$$TiO_2 + h\nu(UV) \longrightarrow TiO_2(e^-_{Cb}) + TiO_2(h^+_{Vb}) \ldots\ldots\ldots(1\text{-}21) \qquad (1)$$

$$TiO_2\,(h^+_{Vb}) + H_2O_{ads} \longrightarrow TiO_2 + {}^{\bullet}OH_{ads} + H^+ \ldots\ldots\ldots(1\text{-}22) \qquad (2)$$

$$TiO_2\,(h^+_{Vb}) + OH^-_{ads} \longrightarrow TiO_2 + {}^{\bullet}OH_{ads} \qquad \ldots\ldots\ldots(1\text{-}23) \qquad (3)$$

Generally, as acceptor molecules (A) such as O_2 will be adsorbed and react with an electron in the conduction band, while donor molecules (D) such as water (H_2O) will be adsorbed as well and react with a hole in the valence band [Lomoră M. *et al.* (2011), Cheng C. *et al.* (2012)], as the following equations:

$$TiO_2\,(e^-_{Cb}) + A_{ads} \longrightarrow TiO_2 + A^-_{ads} \ldots\ldots\ldots\ldots(1\text{-}24) \qquad (4)$$

$$TiO_2\,(h^+_{Vb}) + D_{ads} \longrightarrow TiO_2 + D^+_{ads} \ldots\ldots\ldots\ldots(1\text{-}25) \qquad (5)$$

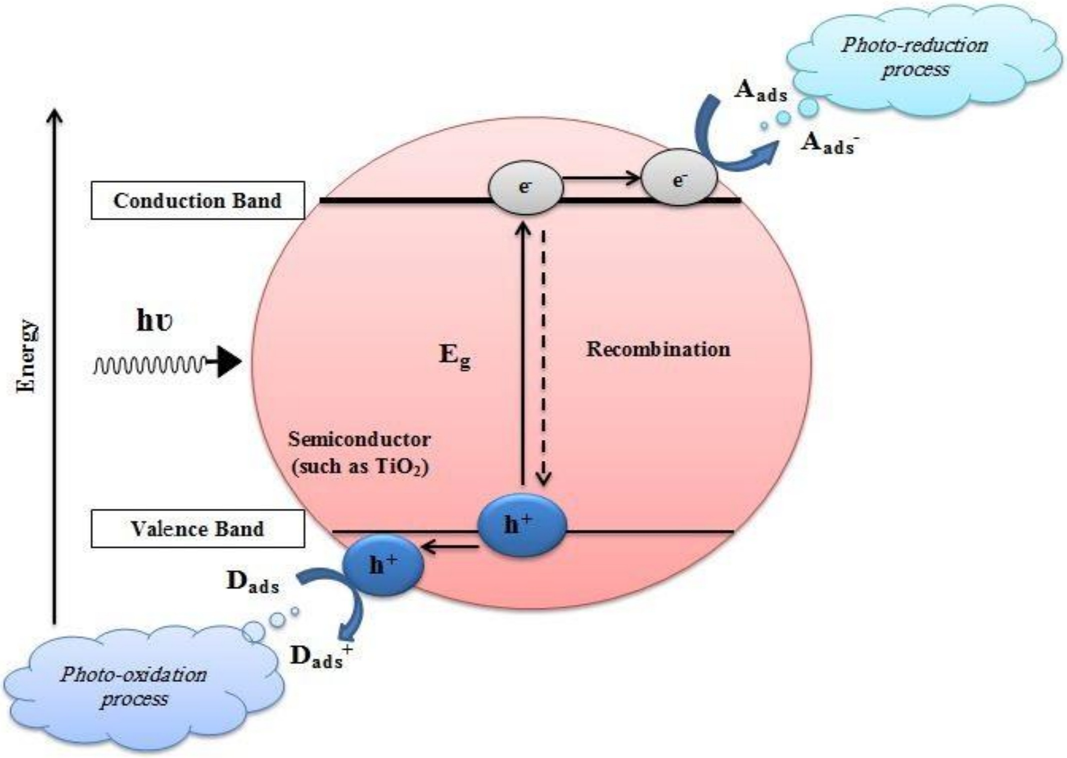

Figure-1- the simplified photocatalytic process on TiO_2 surface.

The advantages of heterogeneous systems are [Sathish (2006)]:

A- Simplicity of separation of catalyst after reaction by centrifuge.
B- Availability of large surface area.
C- Low cost.
D- Stability (no chemical reaction).

In the heterogeneous photocatalytic process not all the semiconductors have high photoactivity, because of the recombination process that occurred between the photohole and photoelectron, so one of the most important remediation methods is the doping of metal on the surface of the semiconductor, the activity can be increased by adding a noble metal or a metal from the transitional series of the periodic table. The metal doped on the surface of the semiconductor acts as a capture for the released electrons by the exerted UV light on the photocatalyst [Julian *et al.* (2003), Dingwang *et al.* (2001), Sakthivel *et al.* (2004)], the electron migrated to the conduction band and then trapped by the metal to avoid the recombination process, while the hole migrates to the surface of the photocatalyst and participates in an oxidation process with the adsorbed water of other organic compounds as the schematic diagrams(2)&(3).

As an example for the metal doped a semiconductor Ag/TiO_2 and Pt/TiO_2 (prepared by the photoreduction deposition process and the chemical vapor deposition "CVD") [Chia (2007)].

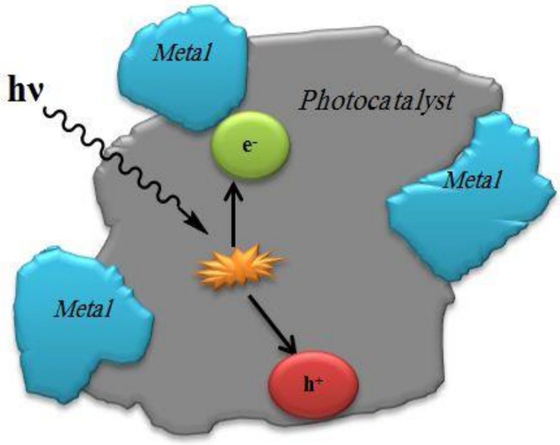

Figure-2- Metal deposition on the surface of the semiconductor and the process of trapping the electron by the metal.

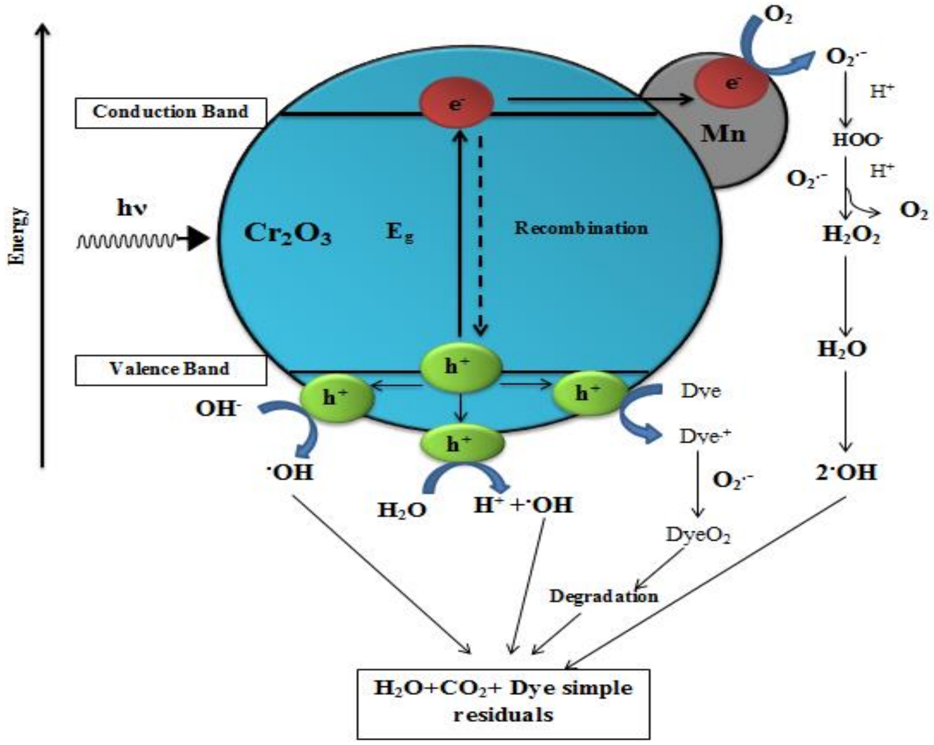

Figure-3- The proposed photocatalytic process on the surface of the metal doped Cr_2O_3 (Mn/Cr_2O_3).

Congo red:

Congo red dye was first synthesized in 1883 by Paul Bottiger who was working then for the Friedrich Bayer company in Elberfeld, Germany. Congo red is considered a pH indicator because it changes of color from blue to red at pH(3.0-5.2) [Bibek (2010)]. Congo red is the sodium salt 3,3’-([1,1’-biphenyl]-4,4’-diyl)bis(4-aminonaphthalene-1-sulfonic acid), its formula is ($C_{32}H_{22}N_6Na_2O_6S_2$) and its molecular weight is (696.66 g/mole) and it is considered a secondary diazo dye because it contains two azo groups (-N=N-) figure-4-, it absorbs the electromagnetic spectrum at λ_{max}=497nm [Pooja M. et al. (2013)].

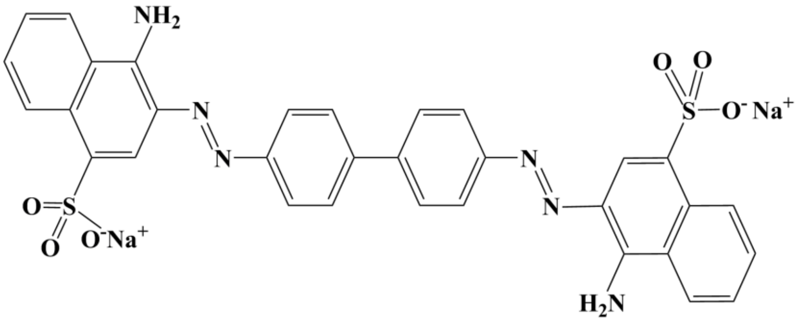

Figure-4- The structure of Congo red.

Lanping Zhang *et al.* (1997) prepared chromium oxide films on Pt(111) with thickness ranging from less than monolayer to more than eight monolayer, they found that chromium oxide grows with two different type structures on the Pt(111) surface depending on coverage and temperature.

Zorica *et al.* (2002) activate by mechanically state for an equimolar of ZnO and Cr_2O_3 powder mixture by grinding using a high vibrational grinder for 0-180 min, and found that the activity of powders increases with increasing the grinding time and this is an indicator for the activity of spinels increase with decreasing of the grain size of the powdered spinel.

Shahid Khan Durrani *et al.* (2012) synthesized some transition nanosized metal chromite spinels by using hydrothermal process and made a characterization by XRD, SEM and thermogravity technique. And found that nanocrystalline transition metal chromite spinels such as $CoCr_2O_4$ (bluish-green), $MnCr_2O_4$ (grayish-green), $Cu_{0.5}Mn_{0.5}Cr_2O_4$ (green), $NiCr_2O_4$ (sage green), $CuCr_2O_4$ (blackish-green), and $Ni_{0.8}Cu_{0.2}Cr_2O_4$ (dark green) were synthesized successfully through a hydrothermal method.

Materials and methods

Manganese(II) nitrate tetrahydrate [$Mn(NO_3)_2.4H_2O$] (Aldrich "purity $\geq$ 97.0 %") and Chromium(III) nitrate nonahydrate [$Cr(NO_3)_3.9H_2O$] (Hopkin & Williams).

Mn/Cr_2O_3 was prepared by Co-precipitation method [Prasad R. et al. (2010)], different percentages of manganese nitrate tetrahydrate $Mn(NO_3)_2.4H_2O$ and Chromium nitrate nonahydrate $Cr(NO_3)_3.9H_2O$ were taken table-1-, dissolved in distilled water and were mixed together and transferred to a beaker (400ml) and filled to the mark with distilled water put on a hot plate magnetic stirrer. The temperature was fixed about (65°C-75°C) with continuous stirrer, NaOH (8N) drop-wise was added to the mixture and the pH maintained by a pH meter at (7.5-9.5), then the obtained precipitate was left on the hot plate for 1 hour with continuous stirrer.

Table-1- Number of moles and percentages of $Mn(NO_3)_2.4H_2O$ and Cr $(NO_3)_3.9H_2O$ that was taken to prepare the catalyst.

Name of photocatalyst	Wt% $Mn(NO_3)_2.4H_2O$	Wt% $Cr(NO_3)_3.9H_2O$	No. of moles of $Mn(NO_3)_2.4H_2O$	No. of moles of $Cr(NO_3)_3.9H_2O$
Cat-1-	60	40	0.06	0.04
Cat-2-	50	50	0.05	0.05
Cat-3-	40	60	0.04	0.06

The obtained precipitate was washed with a hot distilled water for many times in order to eliminate the undesired sodium ions, until pH of obtained washing water close to the neutral medium (pH=7.0) it means that the precipitate is free of sodium ions, and the precipitate was dried in an oven at about (100°c) then the precipitate was triturated in a ceramic mortar to make homogenous particle the precipitate was (green-brown) color Figure-5-.

The calcination process was made in different temperatures (a)550°C and (b)750°C for 4 hours at the atmospheric air, black color precipitate was obtained and was characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM).

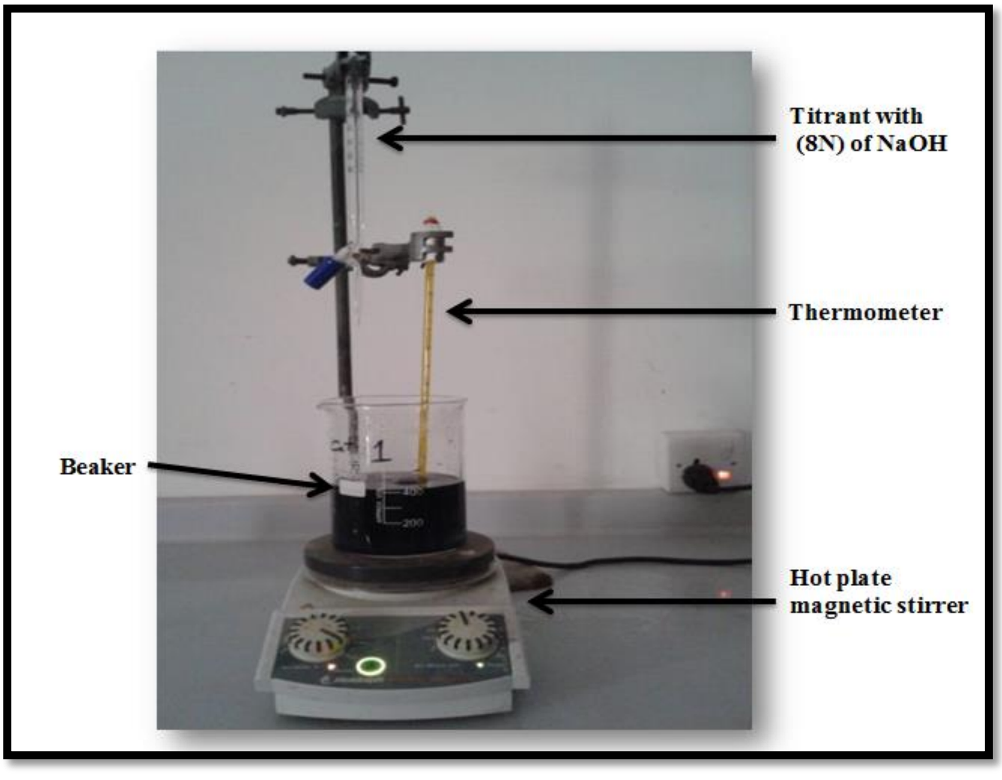

Figure-5- Co-precipitation reactor.

Characterization process:

In this work, the prepared catalysts characterized by using XRD (Rigaku- MiniFlex II Desktop X-ray Diffractometer) and the crystallite size was determined from Scherrer's equation eq.-6-, where it was prepared as a homogenous powder, (1 g) of the catalyst was placed on a slide put in front of the path of the X-ray.

$$\boldsymbol{D} = \frac{\boldsymbol{k\lambda}}{\boldsymbol{\beta Cos\theta}} \quad \dots\dots\dots(6)$$

Where D is mean crystalline size, k is the Scherrer's Constant or that which is called the shape factor because it depends on the shape of the crystal and its value is (0.94), λ is wavelength of the X-ray radiation (0.15406 nm for Cuk_α), β is the full width of half-maximum (FWHM) intensity of the appeared peak explained in radians (Actually, β is measured in degrees but to unitizing the units of the equation β multiple by (π/180) to transmute to the radians and lastly θ is the diffraction Bragg's angle [Riahi-Noori *et al.* (2011)].

Scanning electron microscope(SEM) [INSPECT S50] was used to determine the morphology of the prepared photocatalyst and the crystallography, a bit weight of the catalyst was taken and coated with a thin carbon layer and fixed on a plate and exposed to an electron beam.

Calibration curve:

A solution of Congo red was prepared with a concentration (1000 ppm) in a volumetric flask with (1.0 Liter) volume then series of solutions were prepared with different concentrations (1, 3, 5, 7, 10, 15, 20 and 25ppm) and then measured by the UV-Visible spectrophotometer [UV-1650PC Shimadzu, Japan] and then the spectrum and the calibration curve were drawn.

Applications of the prepared photocatalysts:

Many applications for the prepared photocatalysts were carried out to determine the optimum conditions for photocatalytic degradation of Congo red as a textile dye, by using high pressure mercury lamp (125 watts), with light intensity (7.1 mW/cm^2) at (5cm) distance between lamp and the photocell.

Examination of the photocatalytic activity:

The examining of the photocatalytic activity of the prepared Mn/Cr_2O_3 was made, a (0.1g) of the different prepared photocatalysts was taken with (100ml) of (20ppm) of Congo red, and put in the photoreactor at (298 K) and (7.1mW/cm^2) light intensity at pH7.

Determination of the adsorption time:

To begin the study of the optimum conditions, at the beginning we have to determine the adsorption time of the photocatalysts to insure that most of dye molecules are adsorbed on the surface of the photocatalyst, so for the most active photocatalyst of prepared Mn/Cr_2O_3 (0.07g) was taken with (100ml) of (10ppm) of Congo red at (298K) and (7.1mW/cm^2).

Effect of catalyst's weight on the photocatalytic degradation of Congo red:

This process occurred by making many experiments by using different weights of the photocatalyst (0.03, 0.05, 0.07, 0.1 and 0.25g) respectively, one experiment for each weight alone, then different weights of Mn/Cr_2O_3 were added to (100ml) of Congo red, here is all the other conditions were kept constant such as concentration of Congo red was (10ppm), temperature was (298K), pH=7, light intensity was (7.1mW/cm^2).

Effect of concentration of Congo red with constant weight of Mn-Cr_2O_3:

Different concentrations of Congo red were taken in different experiments (10, 15, 20 and 25ppm) with (0.1g) of Mn/Cr_2O_3 in (100ml) of the dye at (298K), (7.1mW/cm^2) was the light intensity and pH=7.

Results and Discussion

X-ray diffraction of Mn/Cr_2O_3 prepared at different ratios of Mn:Cr_2O_3 and comparison to the metallic Mn and Cr_2O_3:

X-ray diffraction was taken for the prepared photocatalysts that were prepared at different ratios and were calcinated at (550°C) in figure-6-:

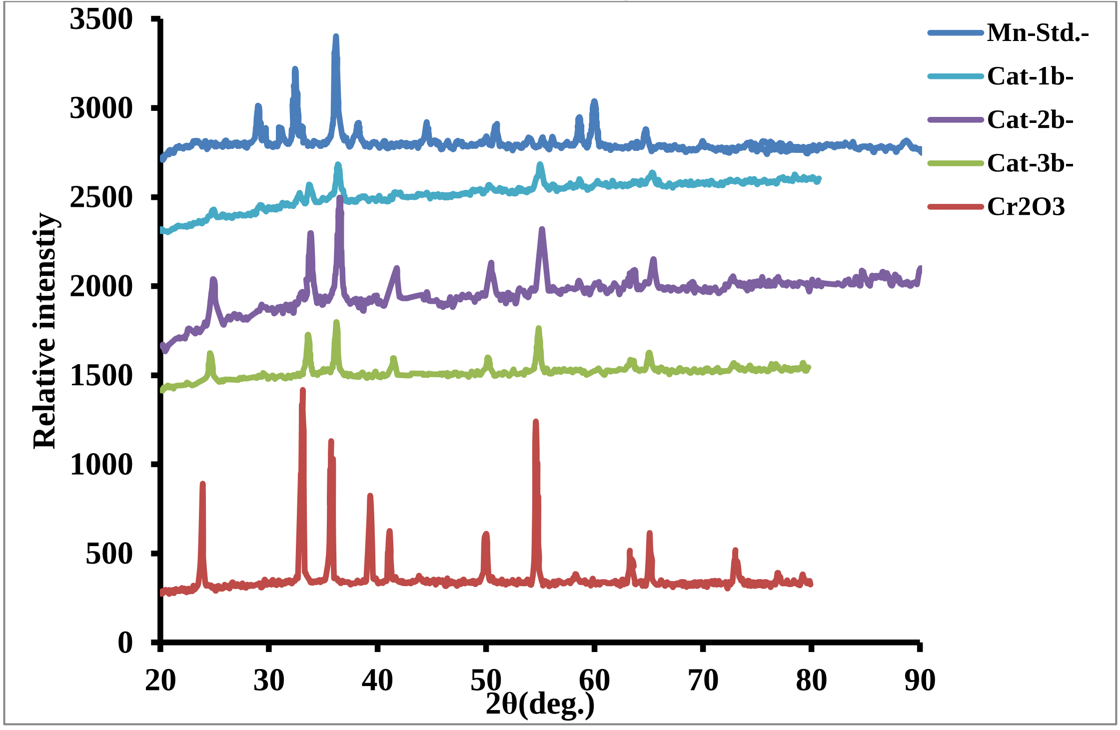

Figure-6-: XRD patterns of Mn/Cr_2O_3 prepared in different percentages and calcinated in (550°C) and compared to Mn(metal) and Cr_2O_3.

Figure-6- is an obvious evidence for the good interface and constitution of Mn/Cr_2O_3 doped-semiconductor and showed the existence of the Cr_2O_3 peaks and the peaks of metallic manganese (Mn) and was a shift in the peaks positions and intensities noticed relative to the formation of a new phase of the semiconductor and is (Mn/Cr_2O_3) mixture of the metal doped on the chromium oxide (Cr_2O_3) surface, where from Figure-6- and for (Cat-1b-) there were the peaks (33.660°, 36.320°, 54.960°, 58.580° and 60.240 °) return to the metallic Mn and (29.240°, 50.260°, 65.280°) return to the Cr_2O_3 and this ratio of catalyst contained more peaks relative for the metallic Mn than those for Cr_2O_3.

And for (Cat-2b-) approximately the same for (Cat-1b-), because it appears peaks at (32.980°, 36.420° and 50.380°) for single Mn and appeared other peaks related to Cr_2O_3 standard at (24.820°, 33.800°, 39.780 °, 41.680°, 55.00° and 65.280°), but there is very little shift in the peak's position and there was an elimination of some peaks the two terminals of the prepared photocatalyst (Mn &Cr_2O_3).

For (Cat-3b-) there were many peaks observed for chromium oxide phase at (24.620°, 33.660°, 39.840 °,41.540 °, 50.260 °, 54.880°, 63.440° and 65.100°), the phase of metallic Mn was just with one peak in the chart of the XRD at (36.260°) that is natural because the Mn percentage was (40%) only.

Calculations of the mean crystallite size of (Mn/Cr_2O_3):

From the X-ray diffraction the mean crystallite size of the Mn doped Cr_2O_3 was calculated and the impact of Mn loaded on the crystallite weight:

Table-2- Impact of the Mn-loaded on the mean crystallite size of the prepared photocatalyst (Mn/Cr_2O_3) at different ratios and calcinated at (550^{o}C) for 4hrs:

Catalyst	2θ	FWHM	D/nm	Average
Mn-1b-	54.96	0.353	26.49	
(60:40)	36.32	0.424	20.59	**23.90**
	65.28	0.4	24.63	
Mn-2b-	36.42	0.376	23.22	
(50:50)	55	0.447	20.92	**21.53**
	33.8	0.424	20.45	
Mn-3b-	36.26	0.353	24.72	
(40:60)	54.88	0.376	24.86	**24.21**
	33.66	0.376	23.05	

And it summarized in the figure-7-:

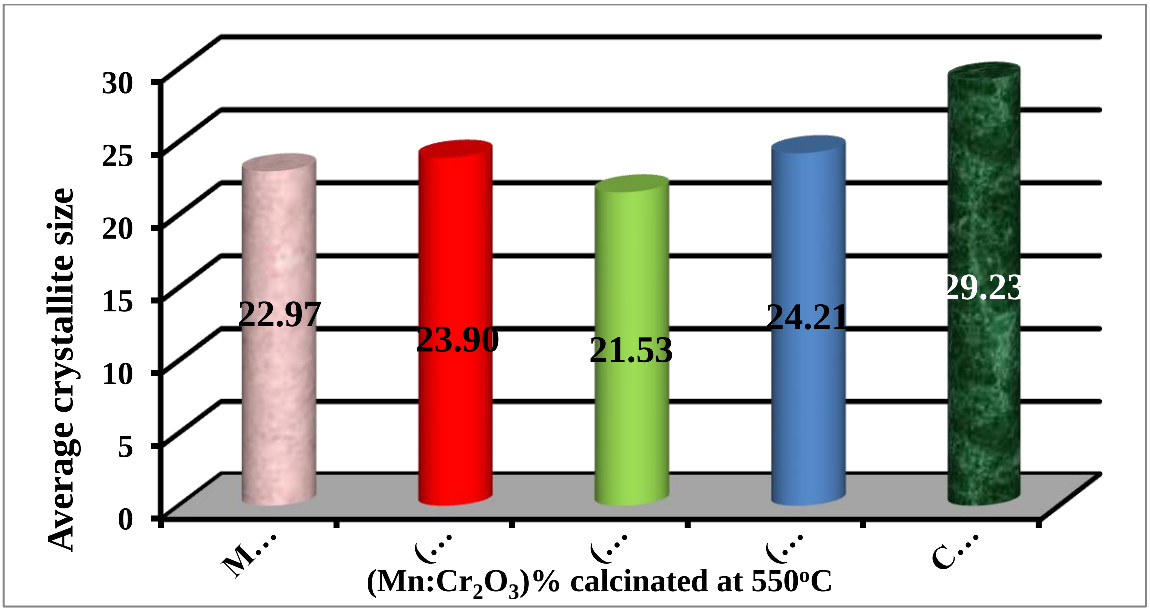

Figure-7- Impact of the Mn-loaded on the chromium oxide on the mean crystallite size of the prepared $Mn-Cr_2O_3$ at different ratios and calcinated at (550^{o}C).

The above figures and tables showed that the increase in the ratio of metallic manganese loaded on the Cr_2O_3, it will decrease the mean crystallite size until the ratio became (50:50)% of ($Mn:Cr_2O_3$)% it will relatively increase, because of the crystallite size of the metallic manganese is relatively smaller than that of Chromium oxide.

Scanning Electron Microscope (SEM):

This technique was used to study the structures of the prepared photocatalysts from the aspect of the morphology of crystals of the semiconductors using the SEM's tip of the electron gun, the prepared photocatalysts $Mn-Cr_2O_3$ were compared with the standard materials (metallic Mn & Cr_2O_3):

From figure-8- below it is obvious that the new phase is placed between the metallic Mn and the chromium oxide in rigidity each one alone. And it is also a heterogeneous shaped due to that it needs for more control and longtime mortaring.

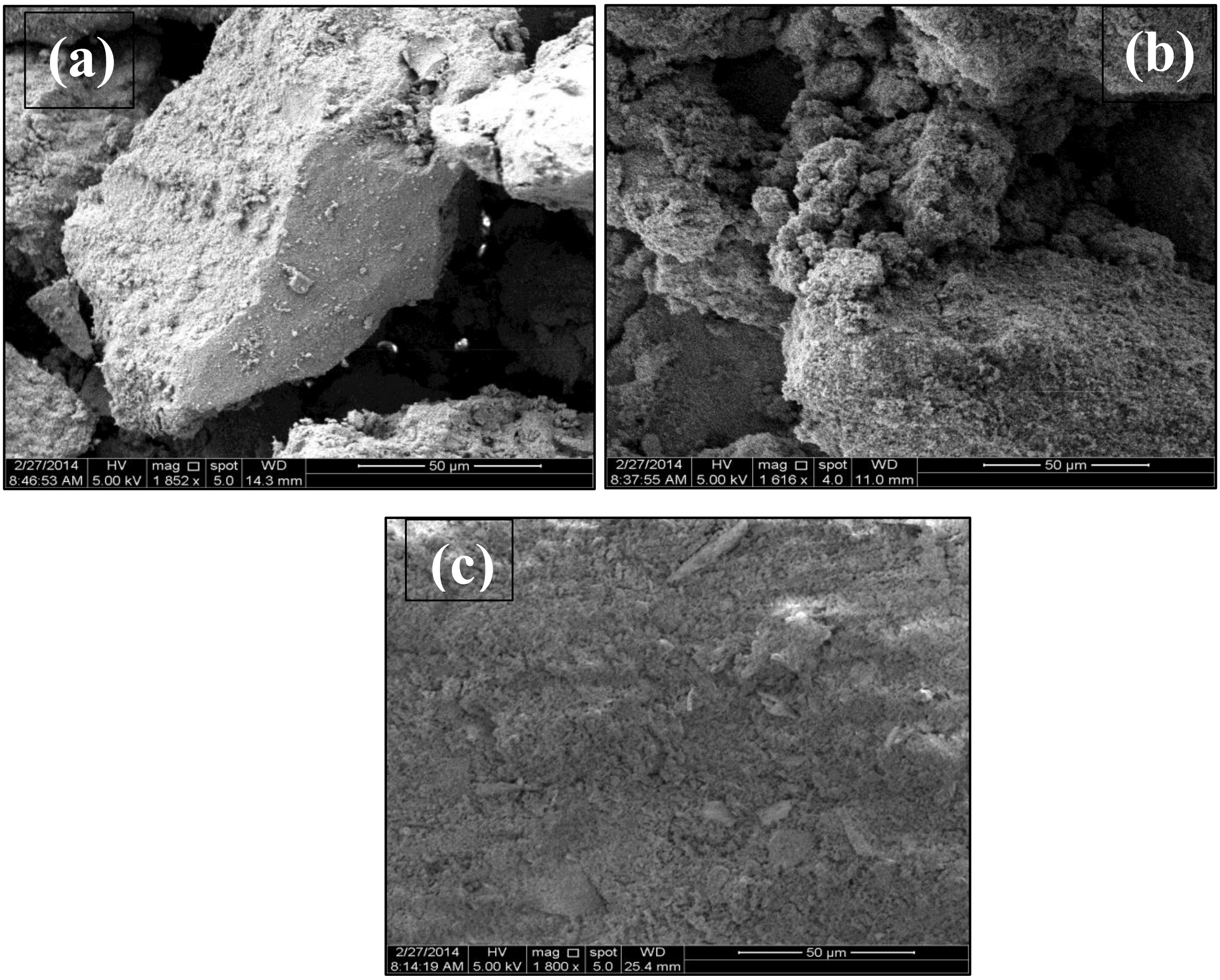

Figure-8- SEM of (a)Mn/Cr_2O_3 (40:60)% calcinated in 550^oC (b) Mn-metal (c) Cr_2O_3.

The plot of the calibration curve showed the limits of the concentration that could be prepared from Congo red without the occurrence of the deviation of Lambert-Beer's law, also to convert the absorbance to the concentration, because the calibration curve is a plot between the absorbance opposite to the concentration, and the most important is to optimize the maximum wavelength (λ_{max}) of Congo red figure-9- and figure-10-.

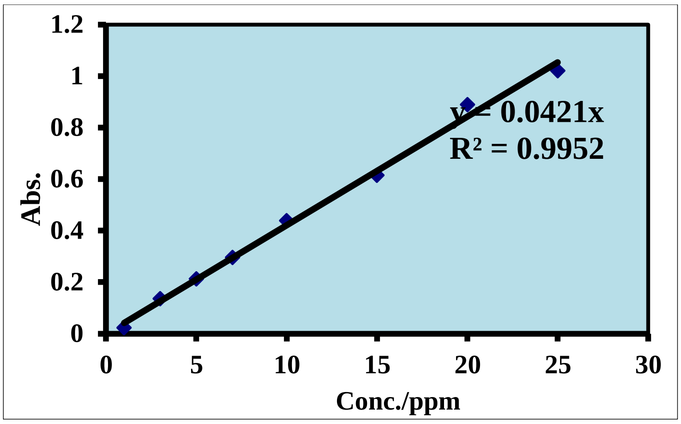

Figure-9- plot of calibration curve of Congo red (Concentration Vs. Absorbance).

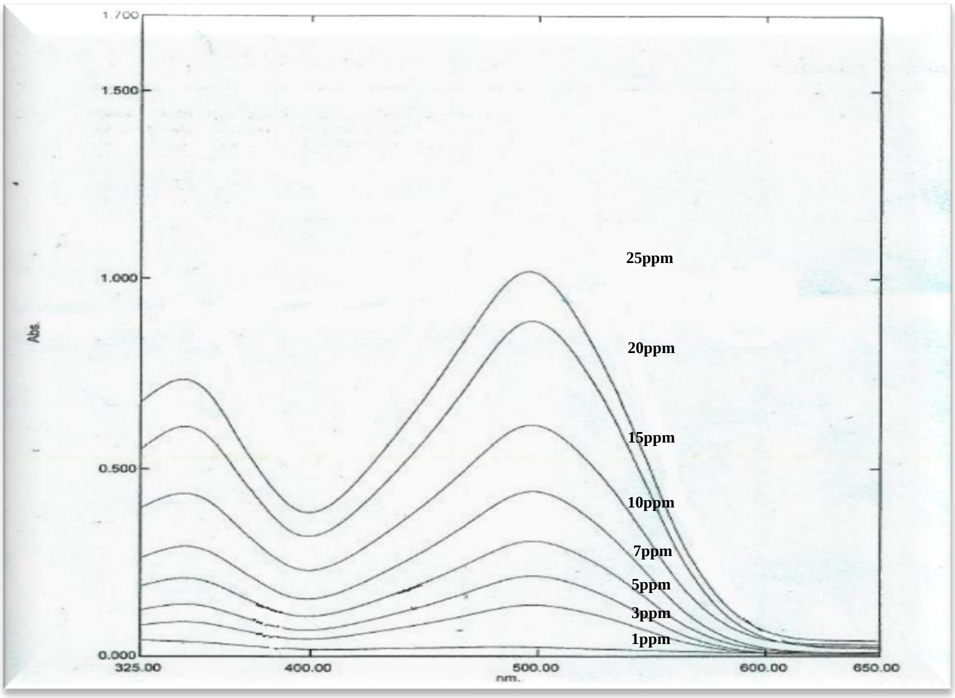

Figure-10- UV-visible spectrum of Congo red.

It is obvious from figure-9- that the concentrations that obeyed the Lambert-Beer's law were (1 ppm – 25 ppm) that were prepared by the dilution equation:

$$\mathbf{ppm_1 * V_1\ (ml) = ppm_2 * V_2\ (ml)\ \ ………..(7)}$$

The accuracy of the calibration curve (R^2= 0.9952) and it was very high. From figure(3-19) it can be concluded that the λ_{max}= 497nm and it agrees with Movahedi M., et. al. (2009) , Tišma M. et, al. (2012). And can convert the absorbance to concentration from the Lambert-Beer's law Skoog D. et. al. (2004), Christian G. D., (2004) & Harvey D., (2000):

$$A = \mathcal{E}bC\ …….(8)$$

A=Absorbance.

$\mathcal{E}$= molar absorptivity= ***slope****= 0.044 $cm^{-1}.mole^{-1}.litre$ from the calibration curve.*

b= the cell thickness and usually= 1 cm.

C= the concentration of the substance.

$$C= A/slope= A/0.044\ \ ………(9)$$

Examining of the photocatalytic activity of the prepared photocatalysts

The photocatalytic activity for the prepared photocatalysts Mn-Cr_2O_3 was determined by the removal percentages as in figure-11-:

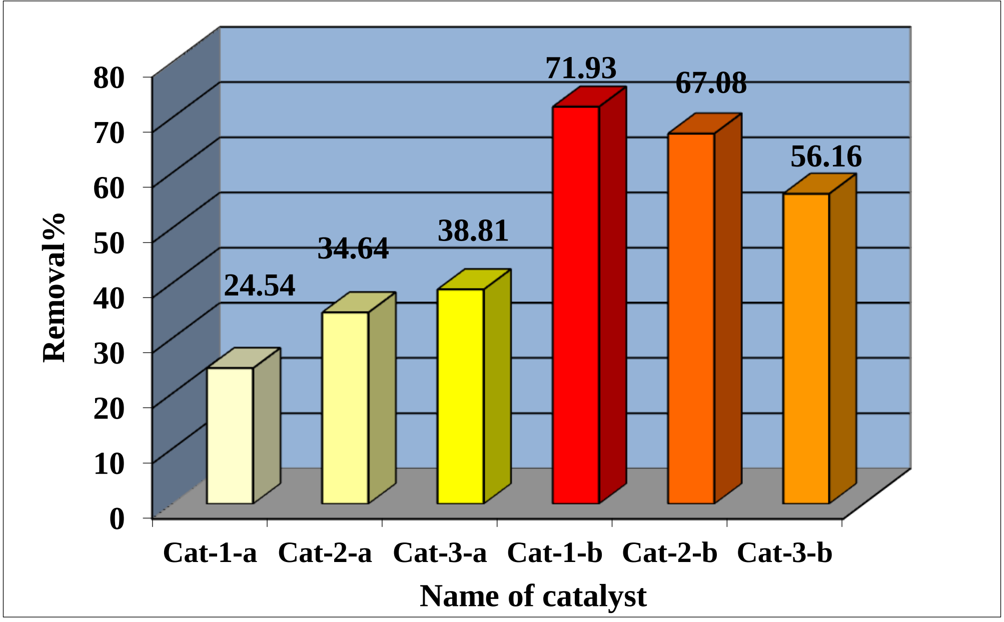

Figure-11- Photocatalytic activity of prepared Mn/Cr_2O_3 (20 ppm of dye and 0.1g of catalyst Mn/Cr_2O_3).

The best photocatalytic activity was determined from the above figure and it was (71.93%) for the sample Cat-1b- that its ratio was (60:40)% of (Mn:Cr_2O_3) and which was calcinated at (550^{o}C), because it gives more electron trappers that is (Mn) for the increase of the photoreaction and decreasing of the electron/hole recombination.

Determination of the adsorption time:

This process is to determine the time that all the dye molecule placed in the active sites and all the active sites are all full, to increase the photocatalytic efficiency by increasing number of degraded molecules of Congo red figure -12-.

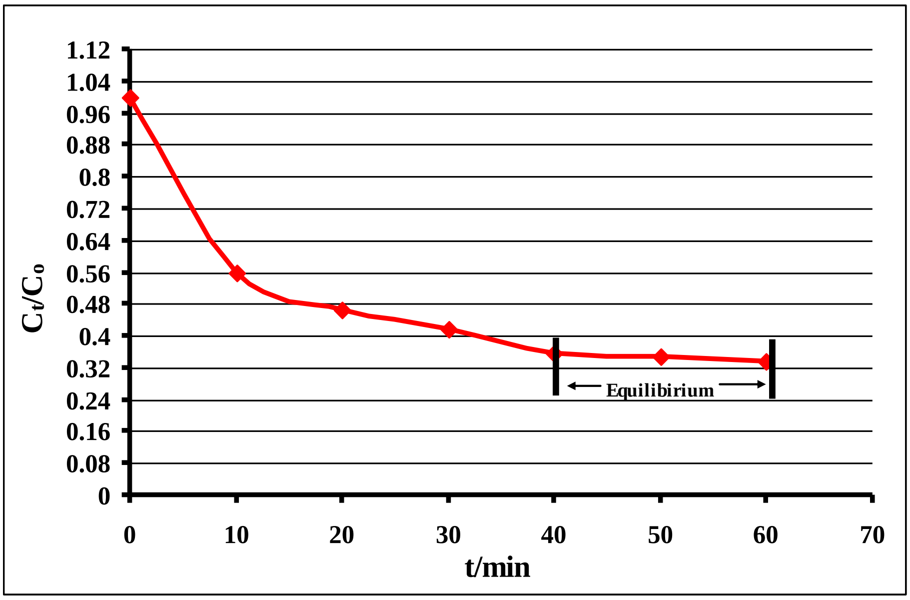

Figure-12- The determining of the adsorption time of the photocatalyst Mn/Cr_2O_3 (Cat-1b-).

It was investigated that the adsorption time of Mn/Cr_2O_3 becomes constant when the time of the adsorption reaction reached (40 minutes) then the adsorption reaction was at an equilibrium state where there was no empty active sites to adsorb the molecules of the dye on the surface of the photocatalyst so the reading of the concentration became approximately fixed.

Effect of the catalyst's weight:

It was notified that the concentration of Congo red approach to zero for each weight of catalyst after (60minutes) of irradiation time and the linear equation relation with the irradiation time and from figure-13- it was notified that the rate of photoreaction increases with increasing the weight of the catalyst in the photoreaction's mixture until reached the tip of the plateau at (0.1 g) and then the rate of photoreaction began decreasing gradually with the increase in the weight of the photocatalyst, where the rate of photoreaction at the plateau region was (0.0443 min^{-1}) as the most rate of photoreaction.

The increasing in the weight of catalyst increases the number active sites available for the adsorption process on the surface of the photocatalyst which increases the number of adsorbed molecules of the dye on the surface of the photocatalyst which increases the number of utilized photons of the incident light and also increase of releasing the number of $^{\bullet}OH$ and $O_2^{\bullet -}$ radicals then the rate of degradation increased, this increment continues until reach the tip of the plateau or the optimum catalyst's mass, then the reaction rate began decreasing with the increase in the weight of the photocatalyst because of the accumulation of an excess number of the photocatalyst's particles(number of adsorbed dye not sufficient to fill the active sites of Mn/Cr_2O_3) which might reduce the transmitted incident UV-light through the solution, so the number of degraded molecules will be decreased then the measured concentration of the dye will be high that which decreases the reaction rate, in general the photocatalytic efficiency depends on the equilibrium between the number of utilized photons and the number of active sites on the surface of the semiconductor, then the excess additional amount of the photocatalyst does not enhance the photocatalytic process [Jain *et. al.* (2006), Ameta *et. al.* (2007), Meena *et. al.* (2009)].

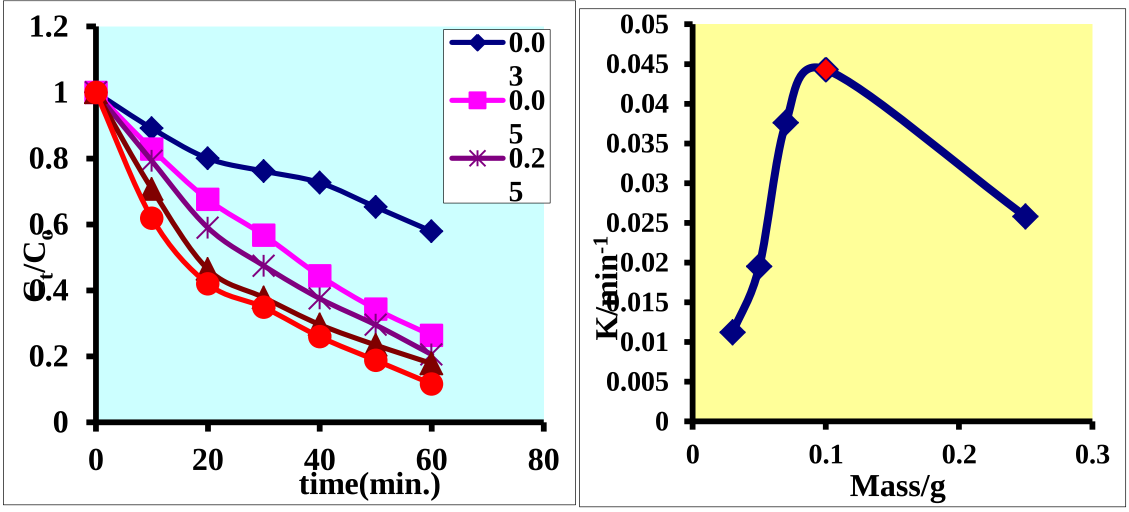

Figure-13- Effect of mass of catalyst on the photocatalytic degradation of Congo red, concentration of Congo red was (10 ppm) with different weights of Cat-1b- of Mn/Cr_2O_3 at pH=7 at temperature (298.15 K) with light intensity (7.1 mW/cm^2).

Effect of the initial concentration of Congo red:

The results listed in indicate that the decomposition rate of the dye depends on the initial concentration of the dye, so when increase of the irradiation time the remaining concentration (C_t/C_o) of Congo red will be decreased at using of Mn/Cr_2O_3 (Cat-1b-) with a weight (0.1 g), but it increases with increasing the taken initial concentration of Congo red from an experiment to another, that means the increase in the initial concentration of the dye decreases the rate of reaction as in figure-14-, when the concentration of the Congo red was (10 ppm) the reaction rate was (0.0443 min^{-1}), but when the concentration of Congo red was (25 ppm) the reaction rate was reduced to (0.0095 min^{-1}) that is absolutely slower than that of concentration of (10 ppm), this behavior returns to that when the molecules of the dye adsorbed on the surface of the photocatalyst the active sites of the photocatalyst it all will be occupied by the adsorbed molecules of dye, but after the addition of an excess number of dye molecules it will be accumulated on the first adsorbed layer of molecules made another layer which is not adsorbed molecules that which affect the utilization of the incident light on the surface and the transmitted light will be reduced because it was well blocked by the accumulated layers of the excess concentration of the Congo red Borhade A. V. et. al. (2012), Samira S. et. al. (2012), Phoacharern, (2006), and Konstantinou I. K. et. al. (2004).

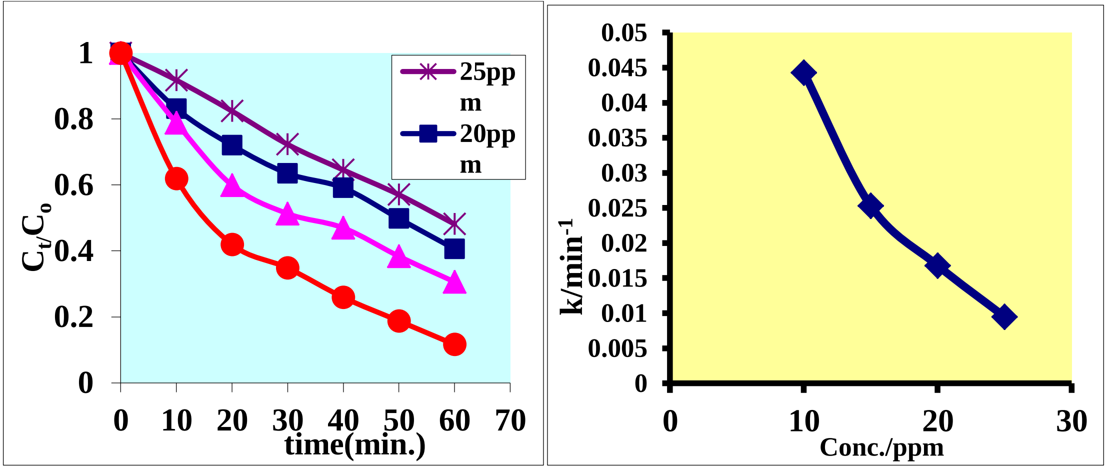

Figure-14- Effect of concentration of Congo red on the photocatalytic efficiency, weights of Cat-1b- of Mn/Cr_2O_3 was (0.1g) at pH=7 at temperature (298.15 K) with light intensity (7.1 mW/cm^2).

Conclusion

Mn/Cr_2O_3 was successfully prepared and characterized by XRD and SEM and with average mean crystallite size **17.97** nm, the best Mn/Cr_2O_3 prepared catalyst in the photoactivity was (Cat-1b-) with percentage (60:40) calcinated at 550°C. From the results we can conclude that the optimum mass of catalyst for Mn/Cr_2O_3 was 0.1g for degradation of Congo red that its concentration was 10ppm at 25°C and 7.1 (mW/cm^2) light intensity.

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